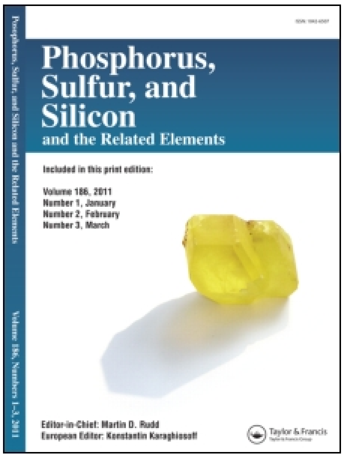

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THE CHEMISTRY OF SOME UREIDOBENZENESULFONYL CHLORIDES

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THE CHEMISTRY OF SOME UREIDOBENZENESULFONYL CHLORIDES

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o-Methoxyphenyl-, N-phenyl-N′,N′-dimethyl, and N-3-acetylphenyl-urea with chlorosulfonic acid gave 4-methoxy-3-ureido, 4-(N′,N′-dimethylureido)-, and N-3-acetylureido-benzenesulfonyl chlorides respectively.

However, attempts to chlorosulfonate phenylthiourea were unsuccessful; the product was the zwitterionic sulfonic acid which did not give the sulfonyl chloride with phosphorus pentachloride.

N-Phenyl-N′-*p*-tolyl urea by reaction with chlorosulfonic acid afforded the corresponding 4-sulfonyl chloride. N-Phenyl-N′-2-pyridyl- and N-phenyl-N′-2-thiazolyl thioureas reacted similarly. In contrast, N-phenyl-N′-2′-pyridylurea only gave the bis-sulfonyl chloride.

Selected ureido-sulfonyl chlorides have been condensed with hydrazine and sodium azide and some reactions of the sulfonyl azides examined.

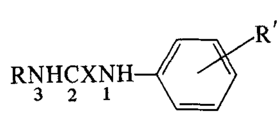
Acetylation of phenylurea gave only the N-(3-acetyl)- or the S-acetyl derivative depending on the conditions. Contrary to previous work, it is not considered that the N-(1-acetyl) phenylthiourea is formed.

INTRODUCTION

Several arylsulfonohydrazides and derivatives are strongly fungicidal;[1,2] furthermore a number of substituted ureas have achieved commercial importance as herbicides.[3] It therefore appeared interesting to obtain further substituted ureidobenzenesulfonyl derivatives for examination as potential biocides. The work described is an extension of previous studies[4,5,6] in this area.

DISCUSSION

Phenylurea (1; X=O, R=R^1=H) can be easily converted[4] to the 4-sulfonyl chloride (2; X=O, R=R^1=H, Y=Cl) by hot excess chlorosulfonic acid.



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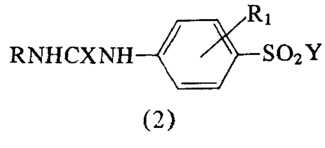

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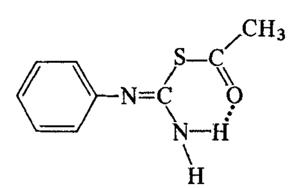

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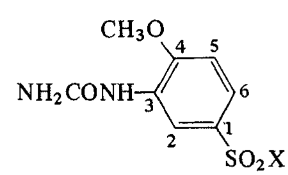

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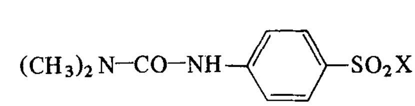

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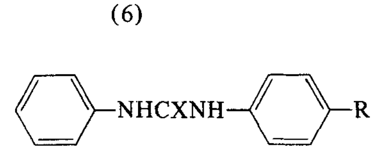

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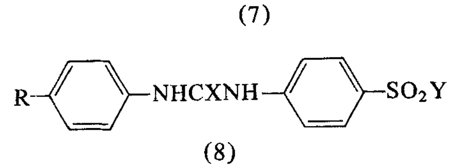

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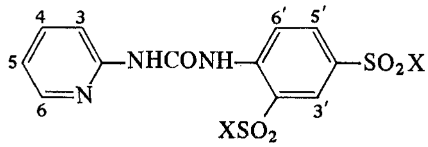
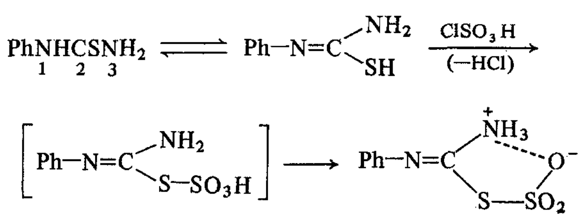


(9)

However, attempts to prepare phenylthiourea-4-sulfonyl chloride (2; X=S, R=R^1=H, Y=Cl) by the same procedure failed. The product, even when drastic conditions (6 mol. equivs. of chlorosulphonic acid at 120–130°, 6 hr) were employed, was phenylthiourea-S-sulphonic acid (3). Subsequent treatment with hot phosphorus pentachloride also failed to yield the sulphonyl chloride (2; X=S, R=R^1=H, Y=Cl). The resistance of phenylthiourea sulphonic acid (3) to conversion to the corresponding sulphonyl chloride is probably due to its existing largely as the zwitterionic structure (3) since it is known[4] that zwitterionic ureidobenzenesulphonic acids sometimes cannot be converted into the corresponding sulphonyl chlorides.

It is suggested that the formation of the sulphonic acid from phenylthiourea probably involves initial reaction of phenylisothiourea with chlorosulphonic acid as follows:



(3)

On the other hand, with phenylurea an analogous reaction *via* the enol form would not be favoured and so normal sulfonation into the aromatic nucleus occurs.

The evidence for the proposed structure of the sulfonic acid (3) is that the i.r. spectrum showed a broad NH stretching band (suggesting NH_3^+), absence of C=S band, and a monosubstituted benzene nucleus. The nmr spectrum indicated the presence of 5 aromatic protons with no *p*-disubstitution pattern. The mass spectrum showed a weak molecular ion (M^+232), supporting the proposed zwitterionic structure (3), and indicated the presence of phenyl and S—SO_3H groups.

The failure to chlorosulfonate phenylthiourea was originally thought to be due to the presence of the reactive amino group, and it was therefore considered that it might be possible to chlorosulfonate the N-acetyl derivative.

According to the literature[7,8,9] there are two acetyl derivatives of phenylthiourea: the N-3-acetyl-(1; R = CH_3CO, X=S, R^1=H), mp 173° and the N-1-acetyl, mp 139°.

We found that when phenylthiourea was dissolved in a large excess of pyridine and treated with an excess of acetic anhydride at room temperature, the product was the N-3-acetyl derivative (1; R = CH_3CO, X=S, R^1=H).

On the other hand, when the reaction was carried out with the thiourea suspended in much less pyridine and using only a slight excess of acetic anhydride, the other acetyl derivative previously claimed to be 1-acetylphenylthiourea was isolated.[7a]

In both cases, the products after purification showed as single spots on thin layer chromatography.

The assignment of the structure of the acetyl derivative (mp 173°) as the N-3-acetyl (1, R = CH_3CO, X=S, R^1=H) appears correct, since the ir spectrum indicated the presence of the thiocarbonyl and the absence of the NH_2 groups.

However the other acetyl derivative (mp 132°), obtained by acetylation under milder conditions, we consider is not N-1-acetyl but the S-acetylthiourea (4) for the following reasons:

On both steric and electronic grounds N(1)-acetylation should prove considerably more difficult than at the N(3)-position; also it is well established[10] that in alkylation reactions of phenylthiourea the S-alkyl derivatives are preferentially formed. So it would be expected that mild conditions of acetylation should favour formation of the S-acetyl derivatives (4), especially since this structure should be stabilized by hydrogen bonding. This formulation is further supported by the ir spectrum of (4) which indicates the presence of NH_2 and absence of the thiocarbonyl groups. An attempt to obtain a diacetyl derivative of phenylthiourea by boiling with acetic anhydride-pyridine was unsuccessful this is in agreement with the observation[10] that only monoacyl derivatives of urea can be made directly. Efforts to chlorosulfonate the two acetyl derivatives of phenylthiourea also failed to give pure products.

Phenylurea is claimed[7b] to give both N-1- and N-3-acetyl derivatives, however we could only obtain the N-3-acetyl derivative (1; R = CH_3CO, X=O, R^1=H) by boiling with acetyl chloride. In contrast to phenylthiourea, attempted acetylation by acetic anhydride-pyridine at room temperature only gave unreacted starting material, as did treatment with sodium hydride followed by acetyl chloride. The enhanced resistance of phenylurea towards acetylation is probably due to the greater deactivation of the amino groups by the stronger electron-withdrawing effect of the carbonyl group.

N-3-Acetylphenylurea has been converted into the 4-sulfonyl chloride (2; R = CH_3CO, X=O, Y=Cl, R^1=H).

Chlorosulfonation of *o*-methoxyphenylurea (1; R = H, X = 0, R^1 = *o* – MeO) gave 4-methoxy-3-ureidobenzenesulfonyl chloride (5; X = Cl) in which sulfonation has occurred *para* to strongest electron donating group (methoxy) this orientation was supported by the nmr spectrum of the amide (5; X = NH_2). The chlorosulfonation of the well-known herbicide Fenuron[11] has been repeated and some further derivatives (e.g., hydrazones, 6; X = NH – N = C R_1R_2 obtained for biological screening (cf. Ref. 6).

In addition the following N-phenyl-N^1-arylureas were synthesized.[12] N-*p*-tolyl (7; X = O, R = Me); N′-2-thiazolyl (1; R = 2-thiazolyl, X = O, R^1 = H); and N′-pyridyl (1; R = 2-pyridyl, X = O, R^1 = H).

The following N-phenyl-N′-arylthioureas were also prepared:[13] N′-2-pyridyl (1; R = 2-pyridyl, X = S, R^1 = H), N′-2-thiazolyl (1, R = 2-thiazolyl, X = S, R^1 = H). Treatment of N-phenyl-N′-*p*-tolylurea (7; X = O, R = Me) with excess of chlorosulfonic acid gave the *p*-sulfonyl chloride (8; R = Me, X = O, Y = Cl).

However, attempted chlorosulfonation of N-phenyl-N′-2-thiazolylurea (1, R = 2-thiazolyl, X = O, R^1 = H) did not give a pure product. In contrast, N-Phenyl-N′-2-pyridylurea (1, R = 2-pyridyl, X = O, R^1 = H) with an excess of chlorosulfonic acid (6 mol. equivs.) afforded the bis-sulfonyl chloride (9; X = Cl).

The structure was proved by conversion into the corresponding bis-sulfonyl azide, hydrazide, and acetone hydrazone. Microanalytical data, obtained for these derivatives indicated that bis-sulfonation had occurred. Furthermore, the mass spectrum of the bis-azide (9; X = N_3) showed the molecular ion (M, 423) corresponding to the structure (9; X = N_3) and fragment ions indicating that both sulfonyl groups were attached to the phenyl ring.

Finally, detailed examination of the nmr spectrum of the bis-acetone hydrazone (9; X = NH-N = CMe_2) showed that there were 7 distinct aromatic protons supporting disulfonation; there were also 4 low field (NH) protons clearly disproving the possibility of N-sulfonation. The values of the individual coupling constants: $J_{3,4}$, $J_{3,5}$, $J_{3,6}$ $J_{4,5}$, $J_{4,6}$, and $J_{5,6}$ were 8.5, 1.0, 1.0, 7.0, 2.0, and 5.0 Hz respectively were in good agreement with the corresponding values obtained for N,N′-dipyridylurea namely: 8.6, 1.0, 1.2, 8.0, 1.8, and 4.8 respectively, proving that sulfonation has not occurred in the pyridine ring.

With chlorosulfonic acid (2 mol. equivs.) no reaction occurred and with 4 mol. equivs. under identical conditions to those used with N-phenyl-N′-2-pyridylthiourea, a low yield of the bis-sulfonyl chloride (9; X = Cl) was isolated.

Treatment of N-phenyl-N′-2-pyridyl (1; R = 2-pyridyl, X = S, R^1 = H), and N-phenyl-N′-1-thiazolyl, X = S, R^1 = H) thioureas with excess of chlorosulfonic acid afforded the corresponding *p*-sulfonyl chlorides (2; R = 2-pyridyl or 2-thiazolyl, X = S, R^1 = H, Y = Cl). The failure of N-phenyl-N′-2-pyridylthiourea to give bis-sulfonyl derivatives with excess chlorosulfonic acid is almost certainly due to greater steric hindrance arising from the larger size of the sulfur atom.

The various ureidobenzenesulfonyl chlorides were converted by standard methods into the corresponding azides, hydrazides, and hydrazones.

Some well-known reactions[14] of sulfonyl azides were examined, such as those with triphenylphosphine, norbornene, and the pseudohalogen displacement of the azido group with butylamine.

Preliminary herbicidal screens have been carried out with several of those compounds using two species of algae *Chlorella pyrenoidsa* and *Anabaena variabilis* in sample test systems similar to those previously used by one of us.[15] Some of the compounds have shown considerable activity as herbicides and the biological results will be reported in detail elsewhere.

EXPERIMENTAL

Ir spectra were recorded as Nujol mulls on an Infracord 237 spectrometer and the nmr spectra were determined with a Varian A60A spectrometer with tetramethylsilane as internal standard.

Mass spectra were recorded with an A.E.I. MS 9 spectrometer operated at 70 eV, by direct insertion probe and using ion chamber temperatures of 120–200°. Microanalyses were by the National Physical Laboratory. Teddington, England. Chromatography was carried out using silica G plates and 10% acetone-benzene as eluant.

Synthesis of Arylureas and Thioureas

The arylureas (1, 7; X = O) were prepared from the appropriate amines by reaction with sodium cyanate as described by Kurzer.[12] The thioureas (1, 7; X = S) were obtained using ammonium thiocyanate following the procedure of Joshua and Rajasekharan.[13]

The following ureas were synthesized:

o-Methoxyphenyl (1; R = H, X = O, R^1 = *o*-MeO) (93%), mp 148–150° (lit.[16] 161–163°). (Found: C, 57.6; H, 5.8; N, 17.1. Calc. for $C_8H_{10}N_2O_2$: C, 57.8; H, 6.0; N, 16.9%). V_{max} 3400 (NH_2), 3390 (NH), 1650 (CO) cm^{-1}.

N-Phenyl-N'-2-Pyridyl (1; X = O, R = 2-pyridyl, R^1 = H) (92%), mp 188° (lit.[17] 187°). V_{max} 3220 (brNH), 1690 (CO) cm^{-1}.

N-Phenyl-N'-p-Tolyl (7; X = O, R = Me) (85%), mp 223° (lit.[18] 219–220°).

N-Phenyl-N'-2-Thiazolyl (1; X = O, R = 2-thiazolyl, R^1 = H) (60%), mp 165° (lit.[19] 173°).

N-Phenyl-N'-2-Pyridyl (1; X = S, R = 2-pyridyl, R^1 = H) (75%), mp 174–175° (lit.[20] 167°). V_{max} 3180 (NH), 1150 (CS) cm^{-1}.

N-Phenyl-N'-2-Thiazolyl (1; X = S, R = 2-thiazolyl, R^1 = H) (80%), mp 178–180° (lit.[21] 178.5°).

4-Methoxy-3-Ureidobenzenesulfonyl Chloride (5; X = Cl) *o*-Methoxyphenylurea (1; X = O, R^1 = *o*-MeO, R = H) (22 g) was heated with chlorosulfuric acid (27 g, mol. equiv.) at 50–55° for 3 hr; the solution was poured onto ice and the solid collected to give the crude sulfonyl chloride (5; X = Cl) (28 g) (80%), mp 110° (decomp.). V_{max} 3450 (NH_2), 3320 (NH), 1660 (CO), 1355, 1150 (SO_2) cm^{-1}. The following sulfonic chlorides were similarly prepared:

p-(3-N-Acetylureido) benzene (2; R = CH_3CO, X = O, R^1 = H, Y = Cl) (67%), mp 183–184°. V_{max} 3265, 3180 (NH) 1730, 1708 (CO), 1350, 1180 (SO_2) cm^{-1}.

N'-4-Tolyl N-Phenylurea-4'-Sulfonyl Chloride (8; R = Me, X = O, Y = Cl) (55%), mp 108°. V_{max} 3340, 3280 (NH), 1340, 1150 (SO_2) cm^{-1}

N'-2-Pyridyl-N-Phenylurea-2',4'-bis-Sulfonyl Chloride (9; X = Cl) (65%), mp 192° (mmp with starting urea = 178–185°, V_{max} 3200 (NH), 1650 (CO), 1350, 1160 (SO_2) cm^{-1}. This was obtained by heating N-phenyl-N'-2-pyridylurea (1; R = 2-pyridyl, X = O, R^1 = H) with chlorosulfonic acid (6 mol. equivs.) at 60–70° for 3 hr. A similar experiment with 4 mol. equivs. of chlorosulfonic acid afforded the bis-sulfonyl chloride (9; X = Cl) in 20% yield.

N'-2-Pyridyl-N-Phenylthiourea-4'-Sulfonyl Chloride (2; R = 2-pyridyl, X = S, R^1 = H, Y = Cl) (69%), mp 200°. V_{max} 3230 (NH), 1380, 1180 (SO_2), 1150 (CS) cm^{-1}.

N'-(2-Thiazolyl)-N-Phenylthiourea-4'-Sulfonyl Chloride (2; R = 2-thiazolyl, X = S, R^1 = H, Y = Cl) (70%), mp 195–198°. V_{max} 3180 (NH), 1350, 1175 (SO_2), 1150 (CS) cm^{-1}.

p-(N',N'-Dimethylureido)-benzenesulfonyl Chloride (6; X = Cl) was obtained as previously described.[6]

Attempted Chlorosulfonation of Phenylthiourea (1; R = R^1 = H) (X = S). Phenylthiourea was heated with chlorosulfonic acid (3 mol. equivs.) at 60–70° for 3 hr to give phenylthiourea sulfonic acid (85%), mp 220°. Other experiments, including the use of chlorosulfonic acid (6 mol. equivs.) at 120° for 6 hr, gave the same product. (Found: C, 35.9; H, 3.3; N, 11.9. The sulfonic acid (3), $C_7H_8N_2O_3S_2$ requires C, 36.1; H, 3.45; N, 12.0%). V_{max} 3490 br (OH, NH_3), 1340, 1150 (SO_2) 730 cm^{-1} (monosubstituted benzene). Nmr δ [$(CD_3)_2SO$] 7.2–8.2, m, 5 ArH; 6.38, s, NH_3.

The mass spectrum showed a weak molecular ion (M^+, 232) and major fragment ions at 215 (M–OH), 199 (M–OH–NH_2), 155 (M–Ph) 119 (–S–SO_3H), 80 (SO_3), 64 (SO_2), 77 (C_6H_5), 50, 51, 48 (SO).

When the sulfonic acid(3) was heated with excess of phosphorus pentachloride at 110–112° for 2 hr, it was recovered unchanged.

N-3-Acetylphenylthiourea (1; R = CH_3CO, X = S, R^1 = H). Phenylthiourea (1; R = H, X = S, R^1 = H) (3.0 g) was dissolved in pyridine (20 ml) and treated with acetic anhydride (20 ml; 10 mol. equivs.). After 12 hr, the product was precipitated by ice-water (100 ml) and recrystallization (methanol) gave the 3-N-acetyl derivative as plates (3.8 g), mp 173–174° (lit.[7a] 173). On chromatography, the product gave a single spot (R_F, 0.85). V_{max} 3120 (NH), 1690 (CO), 1050 (CS) cm^{-1}, Nmr (($CD_3)_2SO$)δ 10.44, 9.70, 2 NH; 7.56, m, 5 ArH; 1.9, s, CH_3. The signals at 10.44 and 9.70 were removed by D_2O treatment.

S-Acetylphenylisothiourea (4). Phenylthiourea (1, R = H, X = S, R^1 = H) (30.4 g) was suspended in pyridine (50 ml) and treated with acetic anhydride (30 g, 1.5 mol. equiv.). The mixture was left overnight and the product recrystallized from methanol to give *S-acetylphenylisothiourea (4)* as needles (38.8 g), mp 132–134° (lit.[7a] 139°). On chromatography the product gave a single spot (R_F 0.80). V_{max} 3300 (NH_2), 1680 (CO) cm^{-1}. Nmr δ (($CD_3)_2SO$) 11.56, 12.78, 2 NH; 7.76, m, 5 ArH; 2.2, s, CH_3.

N-3-Acetylphenylurea (1; R = CH_3CO, X = O, R^1 = H). Phenylurea (1; R = R^1 = H, X = O) (30 g) was boiled with acetyl chloride (34.5 g, 2 mol. equivs.) under reflux for 2½ hr. The excess of acetyl chloride was distilled off and the residual liquid poured onto ice-water. Recrystallization from aq. ethanol gave the 3 N-acetyl derivative as needles (31.5 g, 83%), mp 185–186° (lit.[7b] 183°). V_{max} 3260–3180 (NH) 1730 (CH_3CO), 1690 (NHCONH) cm^{-1}. Nmr δ ($CDCl_3$) 10.4, 2 NH; 7.45–7.20, m, 5 ArH; 2.09, s, CH_3. The signal at δ, 10.4 is removed after D_2O treatment. Chromatography using ether as eluant gave a single spot (R_F 0.84).

4-Methoxy-3-Ureidobenzenesulfonyl Hydrazide (5; X = NH – NH_2). 4-Methoxy-3-ureidobenzenesulfonyl chloride (5; X = Cl) (10 g) was gradually added to a solution of hydrazine hydrate (7.5 g of 98%, 3 mol. equivs.) in ethanol (15 ml) at 0°. The mixture was stirred for 3 hr. diluted with ice-water (200 ml), and the precipitated solid filtered off. Rapid crystallization from methanol afforded the *hydrazide* (5; X = NH–NH_2) (11.5 g, 90% yield), mp 164–165° (Found: C, 36.6; H, 4.9; N, 21.3. $C_8H_{12}N_4O_4S$ requires C, 36.9; H, 4.65; N, 21.5%). V_{max} 3600, 3370, 3290, 3230 (NH), 1665 (CO), 1335, 1140 (SO_2) cm^{-1}.

The hydrazide (5; X = NH–NH_2) was converted into the following hydrazones:†

i) *Acetone* (5; X = NH–N=CMe_2) prisms (44%), mp 166–168° (mmp with the hydrazide 154°).

ii) *p-Nitrobenzaldehyde* (5; X = NH=N=CH · $C_6H_4NO_2$-*p*). Yellow needles (83%), mp 192–193°.

† The analytical and spectral data for these derivatives have been included as a supplementary publication available from the publishers.

iii) *p-Chlorobenzaldehyde* (5; X = NH–N=CH · C_6H_4–Cl · *p*) (75%), mp 168–170° (mmp with hydrazide 154°).

iv) *Cyclohexanone* (5) (67%) mp 163–164° (mmp with hydrazide 146°).

v) *o-Nitrobenzaldehyde* (5; X = NH–N=CH · $C_6H_4NO_2$-*o*), yellow plates (73%), mp 186–188°.

Other Derivatives of 4-Methoxy-3-Ureidobenzenesulfonyl Chloride (5; X = Cl):†

i) *Amide* (5; X = NH_2) needles (80%), mp 184–186°. Tlc (EtOH) single spot (R_F 0.76).

ii) *Anilide* (5; X = NH · C_6H_5) needles (69%), mp 142–143°.

iii) *N-Glycylamide* (5; X = $NHCH_2CO_2H$). The sulfonyl chloride (7, X = Cl) (2.65 g) was reacted with glycine (2.25 g) in water (10 ml) containing 2 N sodium hydroxide (2 ml) overnight to give the *N-glycylamide* as needles (66%), mp 240° (decomp.).

iv) *N-Hydroxylamide* (5; X = NHOH) (76%), mp 156–157°.

v) *Azide* (5; X = N_3). A solution of 4-methoxy-3-ureidobenzenesulfonyl chloride (7; X = Cl) (2.6 g) in acetone (20 ml) was added to a cold solution of sodium azide (1.3 g, 2 mol. equiv.) in water (10 ml). After 3 hr, the solution was poured on ice-water to give the *Sulfonyl azide* (5; X = N_3) (2.25 g) (81%), mp 150–151°.

vi) *N-2-Pyridylamide* (5; X = 2-pyridylamino) (50%), mp 179–181°.

Derivatives of p-(N,N-Dimethylamino) ureidobenzene-sulfonyl Chloride (6; Y = Cl). The hydrazide (6; Y = NH–NH_2) was prepared as previously described[6] and was converted into the following hydrazones:†

i) *Cyclohexanone* (22%), mp 177–178°.

ii) *Ethylmethyl ketone,* (6; Y = NH–N=CMeEt) (45%), mp 187–188°.

iii) *p-Chlorobenzaldehyde* (6; Y = NH–N=CH · C_6H_4Cl-*p*) (90%), mp 174–175°.

Other derivatives obtained included the following N′-substituted sulfonamides (9):†

i) *2-Pyridyl* (6; Y = 2-pyridylamino) (61%), mp 218–219°.

ii) *N′N′-Dimethyl* (6; Y = NMe_2) (82%), mp 170–171°.

iii) *N′,N′-Diethyl* (6; Y = NEt_2) (80%), mp 96–98°.

iv) *N′,N′-Diisopropyl* (6; Y = N $(CHMe_2)_2$) (47%), mp 149–150°.

v) *N′,N′-Di-isobutyl* (6; Y = N $(C_4H_9)_2$) (51%), mp 162°.

p-(N-3-Acetylureido) benzenesulfonohydrazide (2; R = CH_3CO, X = O, R^1 = H, Y = NH–NH_2) (75%), mp 156–157°. (Found: C, 39.5; H, 4.5; N, 20.7.) $C_9H_{12}N_4O_4S$ requires C, 39.7; H, 4.4; N, 20.6%). ν_{max} 3500 (NH_2), 3400, 3320, 3260 (NH), 1705, 1605 (CO), 1335, 1170 (SO_2) cm^{-1}.

The hydrazide was converted into the following hydrazones:†

i) *Acetone* (78%), mp 204° (decomp.).

ii) *Cyclohexanone* (70%), mp 178–180°.

iii) *p-Chlorobenzaldehyde* (90%), mp 220–221°.

iv) *p-Nitrobenzaldehyde* (85%), mp 225–226°.

v) *Glucose* (60%), mp 176°.

Other derivatives of *p*-(3-N-acetylureido) benzenesulfonyl chloride were:

i) *Amide* (2; R = CH_3CO, X = O, R^1 = H, Y = NH_2) (77%), mp 246°.

ii) *Azide* (2; R = CH_3CO, X = O, R^1 = H, Y = N_3) (80%), mp 162° (decomp.).

N′-4′-Tolyl N-Phenylurea-4-Sulfonohydrazide (8; R = Me, X = O, Y = NH–NH_2) (40%), mp 160° (decomp.) (Found: C, 52.2; H, 4.8; N, 17.8. $C_{14}H_{16}N_4O_3S$ requires C, 52.5; H, 5.0; N, 17.5%). ν_{max} 3560 (NH_2), 3330, 3260, (NH), 1350, 1150 (SO_2) cm^{-1}.

N′-2-Pyridyl N-Phenylthiourea-4-Sulfonohydrazide (2; R = 2-pyridyl, X = S, R^1 = H, Y = NH–NH_2) (55%), mp 200–202° mmp with sulfonyl chloride 180–187°. (Found: C, 44.3; H, 3.8; N, 22.0. $C_{12}H_{13}N_5O_2S_2$ requires C, 44.6; H, 4.0; N, 21.7%). ν_{max}, 3380 (NH_2), 3300, 3260 (NH) 1340, 1180 (SO_2), 1140 (CS) cm^{-1}. This was converted into the following hydrazones:

Acetone (2; Y = NH–N=CMe_2) (80%), mp 235° (Found: C, 49.5; H, 4.55; N, 19.3%). $C_{15}H_{17}N_5O_2S_2$ requires C, 49.6; H, 4.7; N, 19.3%). ν_{max} 3300 (NH), 1340, 1180 (SO_2), 1150 (CS) cm^{-1}.

3,4-Dichlorobenzaldehyde (85%), mp 252–255°. (Found: C, 47.6; H, 3.2; N, 14.8. $C_{19}H_{15}Cl_2N_5O_2S_2$ requires C, 47.5; H, 3.1; N, 14.6%).

Azide (2; R = 2-pyridyl, X = S, R^1 = H, Y = N_3) (62%), mp 162° (decomp.). (Found: C, 43.1; H, 2.85; N, 24.8. $C_{12}H_{10}N_6O_2S_2$ requires C, 43.1; H, 3.0; N, 25.2%). ν_{max} 3320, 3280 (NH), 2180 (N_3), 1380, 1175 (SO_2), 1140 (CS) cm^{-1}.

N′-2-Pyridylureidobenzene-2′,4′-bis-Sulfonohydrazide (9; X = NH–NH_2) (79%), mp 182–184° (mmp with the sulfonyl chloride = 168–175°). (Found: C, 35.8; H, 3.5; N, 24.5, $C_{12}H_{15}N_7O_5S_2$ requires C, 35.9; H, 3.8; N, 24.4%). ν_{max} 3420 (NH_2), 3380, 3260 (NH), 1700 (CO), 1340, 1170 (SO_2) cm^{-1}.

The bis-sulfonohydrazide (9; X = NH . NH_2) was converted in the following bis-hydrazones:

Acetone (9; X = NH . N=CMe_2) (86%), mp 192–194° (Found: C, 45.2; H, 5.05; N, 19.9, $C_{18}H_{23}N_7O_5S_2$ requires C, 44.9; H, 4.8; N, 20.4%). ν_{max} 3260 (NH), 1710 (CO), 1350, 1160 (SO_2) cm^{-1}. Nmr $\delta((CD_3)_2SO)$ 0.7–1.0 m, 2XC $(CH_3)_2$ H_5, $J_{3,5} = J_{3,6}$ 1.0, $J_{4,5}$ 6.5, $J_{5,6}$ 5.0 Hz; 1.2, d, 12H, 2XC $(CH_3)_2$

† The analytical and spectral data for these derivatives have been included as a supplementary publication available from the publisher.

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1.8–2.2, d, H_3, $J_{3,4}$ 8.5 Hz; 3.0–3.7, m, H_4, $J_{3,4}$ 8.5, $J_{4,5}$ 7.5, $J_{4,6}$ 2.0 Hz; 4.1–4.5, m, H'_5, $J'_{3,5}$ 2.0, $J'_{5,6}$ 9.5 Hz; 4.9–5.3, m, H_6, $J_{3,6}$ 1.0, $J_{4,6}$ 2.0, $J_{5,6}$ 5.0 Hz; 5.5, s, H'_3, $J'_{3,5}$ 2.5 Hz; 5.6–5.9, d, H'_6, $J'_{5,6}$ 9 Hz; 8.8, m, 3H, $2SO_2NH$, 1NH; 9.8 1H, pyridyl-NH. The signals at 8.8 and 9.8 were removed by treatment with D_2O.

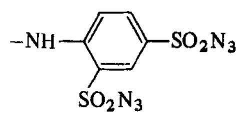
p-Nitrobenzaldehyde (9; X = NH–N=CH–$C_6H_4NO_2$-*p*) (90%), mp 241–243° (Found: C, 46.7; H, 3.51; N, 19.1. $C_{26}H_{21}N_9O_9S_2$ requires C, 46.8; H, 3.2; N, 18.9%). V_{max} 3320, 3260 (NH), 1700 (CO), 1350, 1140 (SO_2) cm^{-1}.

Other derivatives prepared were:

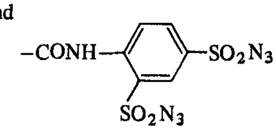
Bis-amide (9; X = NH_2) (70%), mp 200° (Found: C, 39.0; H, 3.3; N, 18.5. $C_{12}H_{13}N_5O_5S_2$ requires C, 38.8; H, 3.5; N, 18.9%).

Bis-azide (9; X = N_3) (63%), mp 153–154° (Found: C, 34.5; H, 2.4; N, 29.4; S, 15.3%). $C_{12}H_9N_9O_5S_2$ requires C, 34.0; H, 2.1; N, 29.8; S, 15.1%).

The mass spectrum shows the molecular ion (M^+, 423) and major fragment ions at 381 ($M-N_3$) and 317 ($M-N_3-SO_2$); there were also peaks at 302 and 330 corresponding to the fragments:



and



respectively.

N-Phenyl N'(2-Thiazolyl) thioureidosulfonyl Azide (2; R = 2-thiazoyl, X = S, R^1 = H, Y = N_3) (72%), mp 145–147° (decomp.). (Found: C, 34.95, H, 2.15, N, 24.3. $C_{10}H_8N_6O_2S_3$ requires C, 35.2; H, 2.35; N, 24.7%). V_{max} 3200 (NH), 2150 (N_3), 1340, 1180 (SO_2) cm^{-1}.

Reactions of the Sulfonyl Azides

i) *With Triphenylphosphine.* 4-Methoxy-3-ureidobenzenesulfonyl azide (5; X = N_3) (2.7 g) was boiled under reflux with a solution of triphenylphosphine (2.6 g, 1 mol. equiv.) in tetrahydrofuran (20 ml) for 4 hr. The solvent was removed under reduced pressure and the residue recrystallized from ethanol to give *triphenyl 4-methoxy-3-ureidobenzenesulfonimino-phosphorane* (5; X = N=PPh_3) (20%), mp 174–176°. (Found: C, 61.6; H, 4.9; N, 8.0. $C_{26}H_{24}N_3O_4PS$ requires C, 61.8; H, 4.75; N, 8.3%). V_{max} 3420, 3380 (NH) 1680 (CO), 1380, 1180 (SO_2) cm^{-1}. Attempted reaction of N-pyridyl-N'-benzene-2',4'-bisulfonyl azide (9; X = N_3) with triphenylphosphine (5 hr in boiling tetrahydrofuran) was unsuccessful.

ii) *With norbornene.* The sulfonyl azide (5; X = N_3) (2 g) was boiled under reflux with norbornene (0.7 g, 1 mol. equiv.) in tetrahydrofuran (25 ml). Evaporation and three recrystallizations from ether gave *4-methoxy-3-ureidobenzenesulfonaza-tricyclo* [3,2,1,$0^{2,4}$]*-octane* (1.3 g, 52%), mp 185–187°. (Found: C, 53.65; H, 5.5; N, 12.3. $C_{15}H_{19}N_3O_4S$ requires C, 53.4; H, 5.65; N, 12.45%). V_{max} 3450, 3380 (NH), 1685 (CO), 1350, 1170 (SO_2) cm^{-1}. Nmr δ ($CDCl_3$) 8.92, d, 1H, ArH_2; 8.45, s, CONH; 7.52, 7.50, d, d, 1H, ArH_5 o/p-coupling, J = 5 Hz; 7.3, d, 1H, 1 ArH_6 *o*-coupling, J = 4 Hz; 6.5, s, $CONH_2$; 4.02, OCH_3; 3.42, 8H, norbornene ring protons; 2.92, s, 2H, bridgehead CH_2. The signals at 8.45 and 6.5 were removed after D_2O treatment. *p-(N,N-Dimethylureido)benzenesulfonazotricyclo* [3,2,1,$0^{2,4}$]*-octane.* This was similarly prepared from *p*-(N,N-dimethylureido)benzenesulfonyl azide (6; X = N_3) and norbornene in (40%) yield, mp 178–181°. (Found: C, 56.8; H, 6.3; N, 12.55. $C_{16}H_{21}N_3O_3S$ requires C, 57.2, H, 6.25; N, 12.5%). V_{max} 3380 (NH), 1670 (CO), 1360, 1165 (SO_2) cm^{-1}. Nmr δ ($CDCl_3$) 8.98, s, CONH; 7.93, s, 4 ArH; 3.42, s, N $(CH_3)_2$; 3.05, s, 8H, norbornene ring protons; 2.92, s, 2H, bridgehead CH_2.

iii) *Attempted Reaction of 4-Methoxy-3-Ureidobenzene-sulfonyl Azide (5; X = N_3) with Butylamine.* The sulfonyl azide (5; X = N_3) (2 g) was boiled under reflux with butylamine (15 ml) for 6 hr, but only the unchanged azide (1.8 g) was isolated.

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